NATIONAL AIR INTELLIGENCE CENTER
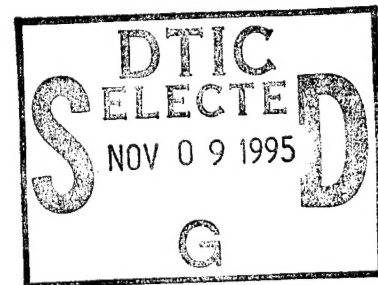
A REVIEW OF RESEARCH ON RED FLUORESCENCE IN COIL CAVITY

by

Cui Tieji, Xie Xingbin, et al.

DTIC
SELECTED
NOV 0 9 1995
G

19951108 026

HUMAN TRANSLATION

NAIC-ID(RS)T-0365-95   4 October 1995

MICROFICHE NR: 95C000621

A REVIEW OF RESEARCH ON RED FLUORESCENCE IN COIL CAVITY

By: Cui Tieji, Xie Xingbin, et al.

English pages: 11

Source: Qiangjiguang Yu Zizishu, Vol 5, Nr. 4,
          November 1993; pp. 498-504

Country of origin: China
Translated by: Edward A. Suter
Requester: NAIC/TATD/Dr. James Newton
Approved for public release; distribution unlimited.

Accesion For		
NTIS CRA&I		☒
DTIC TAB		☐
Unannounced		☐
Justification		
By		
Distribution /		
Availability Codes		
Dist	Avail and / or Special	
A-1		

GRAPHICS DISCLAIMER

All figures, graphics, tables, equations, etc. merged into this
translation were extracted from the best quality copy available.

/498[1]

A REVIEW OF RESEARCH ON RED FLUORESCENCE IN COIL CAVITY
(Translation of "Yangdian Huaxue Jiguang Qiang Zhong Chanshengde
Hongse Yingguang Yanjiu Zongshu")

Cui Tieji, Xie Xingbin, Yang Heping, Qin Yong, Min Xiangde,
Zhuang Qi and Zhang Cunhao
(Dalian Institute of Chemical Physics, Academia Sinica,
P.O. Box 110, Dalian 116023, China)

Abstract: In 1989, S. Yoshida first discovered the red fluorescence phenomenon. Because of its potential to be developed into a visible-light laser, many research teams have made thorough studies of it. Through experimentation, it has become clear that both visible light and near-infrared wavelength radiation are caused by emission of $CuCl_2$ [cupric chloride] in different states of excitation.

Key Terms: $CuCl_2$, red fluorescence

1. The discovery of red fluorescence

In 1989, when S. Yoshida was carrying out a light test with an experimental chemical oxygen iodine laser (COIL) apparatus[1], he first discovered an odd, intense red fluorescent radiation phenomenon[2] around the cavity of the heated aluminum iodine injector tube (see the hatched portion in Figure 1 on the next page), which was accompanied by weak near-infrared radiation. He proposed an initial hypothesis about this emitter of red fluorescence. At first, he believed that the red fluorescence took place because the injection of iodine caused two $O_2(^1\Delta_g)$ [molecules] to combine through van der Waals forces to form a dimer which, when it returned to its ground state, produced red fluorescent radiation. This reaction formula is

---

[1] Numbers on the extreme right represent the page numbers of the original document.

$$O_2(^1\Delta_g) + O_2(^1\Delta_g) + M \rightarrow [O_2(^1\Delta_g)]_2 + M$$

$$[O_2(^1\Delta_g)]_2 + M \rightarrow 2O_2(^3\Sigma_g) + M + h\nu$$
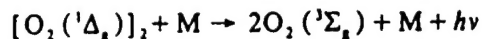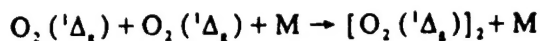
Afterwards, Yoshida only used heated aluminum tubes or other metal tubes, such as copper tubes, which also produced similar red fluorescent radiation spectra. Of these, the red light produced by copper was the most intense. Yoshida discovered that the radiation spectrum's peak interval was 200–300 cm^{-1}, and believed that this was produced by the resonance structure formed by the transition of a stable O_4 molecule whose upper state was a bound state and whose lower state was a repellent state. This may have produced lasing in imitation of the principles of the excimer laser. Yoshida observed lasing output of several dozens of microwatts in his experimental apparatus. Thus, the red fluorescence phenomenon has received a corresponding amount of attention.
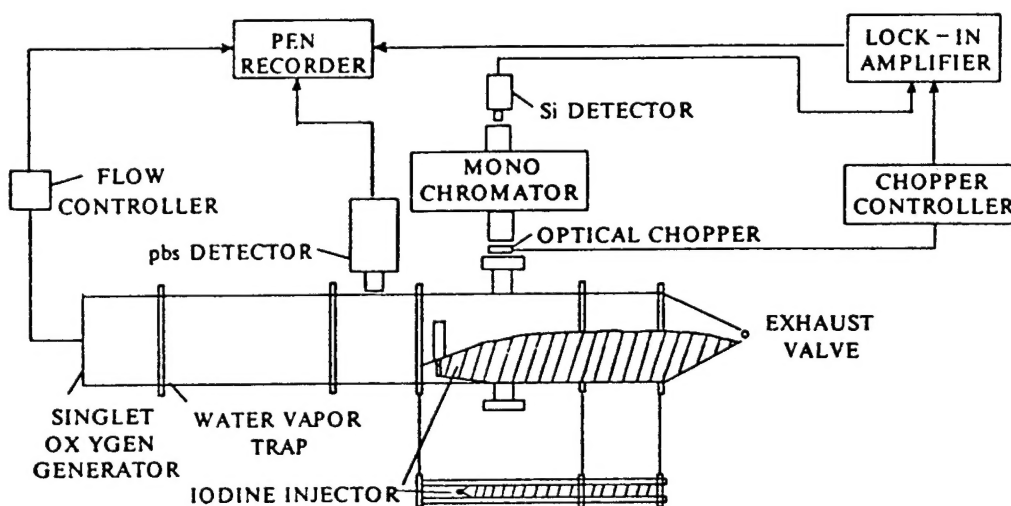

Figure 1. Experimental COIL apparatus. The hatched portion represents the location where the red emission was observed.[2]

---

[2] Note that Figure 1 was originally on page 498.

2. A discussion of luminescence mechanisms

Q. Zhuang et al.[3,7] modified a COIL experimental apparatus so that it would be more suited for researching red fluorescence. They used many kinds of metal materials to make differently-structured intensifiers, and carried out an investigation of their effectiveness at producing red fluorescence. The relative intensity ratio of red fluorescence produced by some of the metals was Ni: Au: Pt: Cu = 1: 2.7: 3.7: 356. Q. Zhuang et al. measured the population density of red light emissions at $2 \times 10^{11}/cm^3$. By contrasting the interactions of microwave generation and drum immersion[3] generation with $O_2(^1\Delta_g)$ and metallic copper, they discovered that the existence of chlorine gas, heated metal, and $O_2(^1\Delta_g)$ is a necessary precondition for the production of red luminescence. The fluorescence spectra produced by the different metal materials (such as nickel, platinum, copper, silver, gold, and tungsten) that were used to make intensifiers were similar. Q. Zhuang et al. also proposed tentative ideas for red fluorescence emitters that may exist.
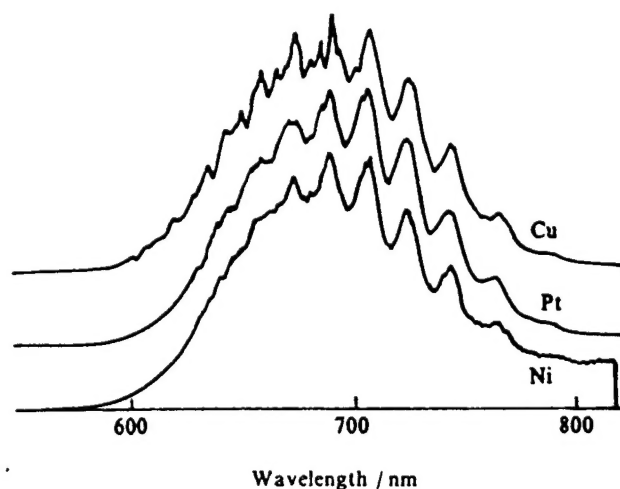
Figure 2. Red fluorescence spectra from different intensifiers

N. P. Vagin[4] proposed that IC1 must be a red fluorescence emitter.

R. Huang[5] put forward conclusions similar to those of document [3], saying that it must be that the red fluorescence emitter does not contain metal atoms from the intensifier, but instead must be a compound of chlorine and oxygen that possesses a certain kind of structure. When lasing experiments on red fluorescence were done in document [5], no

---

[3] No translation found for "*gupao shi.*" It can be literally translated as "drum immersion" or "drum bubble."

lasing phenomenon was discovered. Thus, Huang suspected that the lasing output of several dozens of microwatts mentioned in document [2] was probably brought about by accidental errors in measurement.

In documents [6], [13], and [15], T. Cui et al. made Fourier transform spectrum [measurements] of the visible light portion (resolution ratio $0.1cm^{-1}$) and the near-infrared portion (resolution ratio $0.3cm^{-1}$) of the red fluorescence (see Figures 3 and 5). They also listed the spectrum peak tables different authors obtained using different methods, different resolution ratios, and different apparatuses. Document [10] also surveyed similar spectrum graphs. Under these experimental conditions, [the red fluorescence] was not found to have a finer spectral structure. Its peak intervals were $370–380cm^{-1}$ in the visible range of the spectrum. But the peaks in the short wavelength band were not as clear as those in the long-wave band, having peak intervals of $360–380cm^{-1}$. They also discovered that the contour structure of the spectrum graph is unrelated to testing methods, resolution ratio, and the intensifier used.
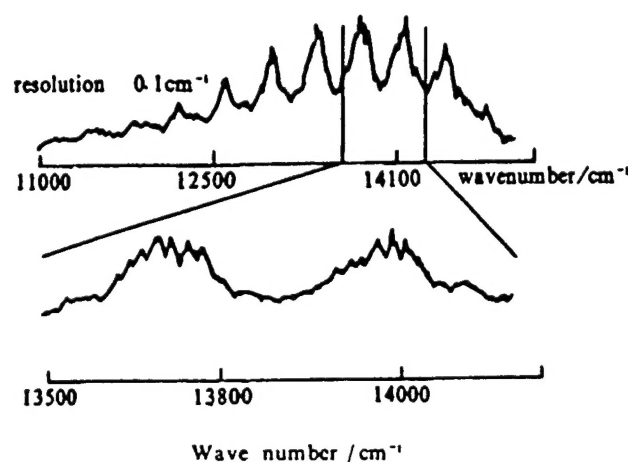

Figure 3. Red fluorescence spectra measured by Bomem FT spectrometer

Documents [8] through [17] described thorough studies of the red fluorescence phenomenon. In them, T. Tokuda[8] and R. Bacis[9] did analyses and assignments of the red fluorescence emission spectrum, and came to the conclusion that it was very possibly the emission spectrum of cupric chloride ($CuCl_2$). A.J. Bouver[11], using a krypton ion laser at 676.4nm and 647.1nm as a $CuCl_2$ LIF [laser interference filter], obtained a Fourier transform spectrum with a resolution ratio of $2cm^{-1}$. [This] further verified the above conclusions. When J. Lamarre[12] used pure platinum, aluminum, and gold metal containing only several millionths of copper foreign matter for red fluorescence emission spectrum

4

contrast experiments, he discovered only visible light spectrum [emissions], but no near-infrared spectrum [emissions]. Therefore, these experimenters proposed that $CuCl_2$ was the emitter of the near-infrared spectrum. The emitter of the visible light spectrum, however, was not $CuCl_2$, even when the intensifier was made of copper.

3. Analysis and conclusions

H.P. Yang et al. used lasers at 635nm and 643nm produced by XeCl maser pumping DCM [dielectric cavity maser] dye to carry out a $CuCl_2$ LIF spectrum experiment (see Figure 4). They discovered that there were two sequences of $370cm^{-1}$ intervals in the dispersion fluorescence spectra. The first, at the shortwave end, had narrower peaks. Its peak position changed according to movements in pumping laser wavelength, and its amount of change was the same. The second, at the long-wave end, had wider peaks, and its peak position did not vary according to movements in pumping laser wavelength. When the pumping laser wavelength was 643nm, the two sequences coincided, and their peak positions were identical (see Table 1). This happened because both sequences were produced by $CuCl_2$ $^2\Pi_u \rightarrow {}^2\Pi_g$ transitions. The LIF sequence that changed along with laser wavelength was a fluorescence signal that had not yet encountered relaxation. The LIF sequence that did not vary along with laser wavelength changes was a fluorescence signal that had encountered relaxation. Thus, the luminescence mechanism for the visible light portion of the red fluorescence should be: the residual chlorine gas in the $O_2(^1\Delta_g)$ generator undergoes a reaction with the copper (even trace amounts) in the surface of the hot metal, which produces ground state $CuCl_2$, part of which changes into gaseous-phase $CuCl_2$ under conditions of high temperature and low atmospheric pressure. It then undergoes relay collision energy transfer with the $O_2(^1\Delta_g)$, producing electron excited-state $CuCl_2$, which then produces visible-light wavelength red fluorescence radiation. Its reaction formula is

/501

$$Cu + Cl_2 \rightarrow CuCl_2\,(^2\Pi_g)$$
$$CuCl_2\,(^2\Pi_g) + O_2\,(^1\Delta_g) \rightarrow CuCl_2\,(^1\Delta_g) + O_2\,(^3\Sigma_g)$$
$$CuCl_2\,(^2\Delta_g) + O_2\,(^1\Delta_g) \rightarrow CuCl_2\,(^2\Pi_u) + O_2\,(^3\Sigma_g)$$
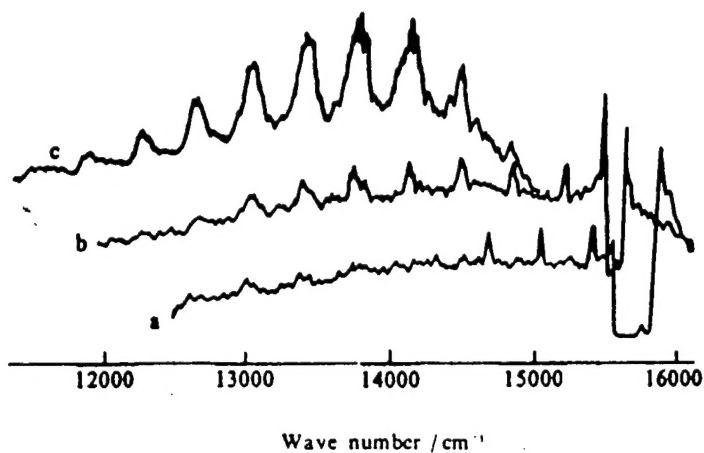$$CuCl_2\,(^2\Pi_u) \rightarrow CuCl_2\,(^2\Pi_g) + h\nu$$

5

Wave number / cm⁻¹
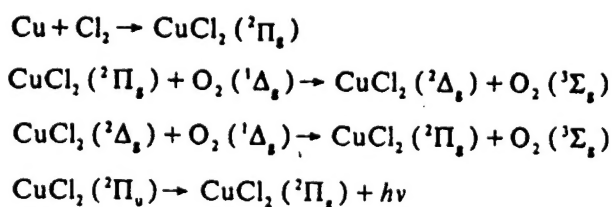
Figure 4. CuCl₂ LIF spectra and red fluorescence Fourier transform (FT) spectrum. Lines a and b represent CuCl₂ LIF spectra for pumping laser wavelengths at 635nm and 643nm, respectively. Line c represents the red fluorescence FT spectrum.

Table 1. Comparison of the main peaks of the CuCl₂ spectrum with those of the red emission spectrum

The main peaks of the LIF of CuCl₂ (cm⁻¹)	The main peaks of the red emission (cm⁻¹)
	11075
	11450
	11830
12235	12215
12600	12600
12980	12985
13360	13360
13720	13725
14085	14080
14448	14450
14820	14810
15190	
15550	
15935	

6

The authors of documents [13] and [16] used the relevant $CuCl_2$ absorption spectra and theoretical and calculated results of their predecessors to do more comprehensive analysis and assignment of the near-infrared emission spectrum of the red fluorescence (see Figure 5). They discovered that it comprised three $CuCl_2$ vibration sequences, and that the vibration interband intervals adjacent to each sequence were approximately $370cm^{-1}$. These correspond to the ground state symmetrical stretching vibrations obtained through theoretical calculations. There was an energy difference of about 177.9 cm^{-1} between the first and the second sequences, which belonged to neither its $CuCl_2$ antisymmetrical stretching ($499cm^{-1}$), nor its flexion vibration. But the spin-orbit splitting of its ground state $^2\Pi_g$ was calculated to be $178cm^{-1}$. Therefore, they believed that the first and the second sequences corresponded to, respectively, $^2\Pi_g(1/2)$ and $^2\Pi_g(3/2)$. The interval between the second and third sequences was approximately $486cm^{-1}$, which belonged to the anti-symmetric transition of its $CuCl_2$ molecules. See Table 2 for the assignments of the third sequence. The energy level of the $^2\Delta_g$ of $CuCl_2$ is very close to that of $O_2(^1\Delta_g)$ and can undergo near-resonance [energy] transfer. Thus, it is possible to obtain the reaction formula of the near-infrared radiation of red fluorescent radiation:

$$Cu + Cl_2 \rightarrow CuCl_2 (^2\Pi_g)$$
$$CuCl_2 (^2\Pi_g) + O_2 (^1\Delta_g) \rightarrow CuCl_2 (^2\Delta_g) + O_2 (^3\Sigma_g)$$
$$CuCl_2 (^2\Delta_g) \rightarrow CuCl_2 (^2\Pi_g) + h\nu$$
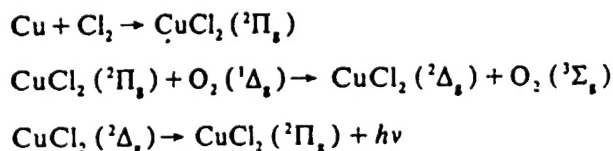
This can explain the phenomenon in the experiment described in document [12] on trace amounts of copper foreign matter where no near-infrared emissions spectrum was observed. Because the total amount of $CuCl_2$ was small, very little of it entered the gaseous state. $CuCl_2$'s transition in the visible wavelength was $^2\Pi_u \rightarrow {}^2\Pi_g$, which is an allowable transition. But its near-infrared wavelength transition was $^2\Delta_g \rightarrow {}^2\Pi_g$, which is a forbidden transition. Thus, near-infrared radiation that exists at the same time as visible wavelength radiation may sometimes be so weak that it is difficult to distinguish. This viewpoint was later confirmed by the experiments of J. Lamarre[17].

The red fluorescence phenomenon produced in chemical oxygen iodine laser cavities has aroused the interest of scientists in China and other countries. Today, experiments have proved that the emission spectrums of its visible and near-infrared wavelengths are caused by $CuCl_2$'s transitions to and from different states of excitation. As basic theoretical work,

7

it is possible to further study the vibration structure of $CuCl_2$ molecules, spectrum constants, and the energy transfer dynamics of $CuCl_2$ and $O_2(^1\Delta_g)$.
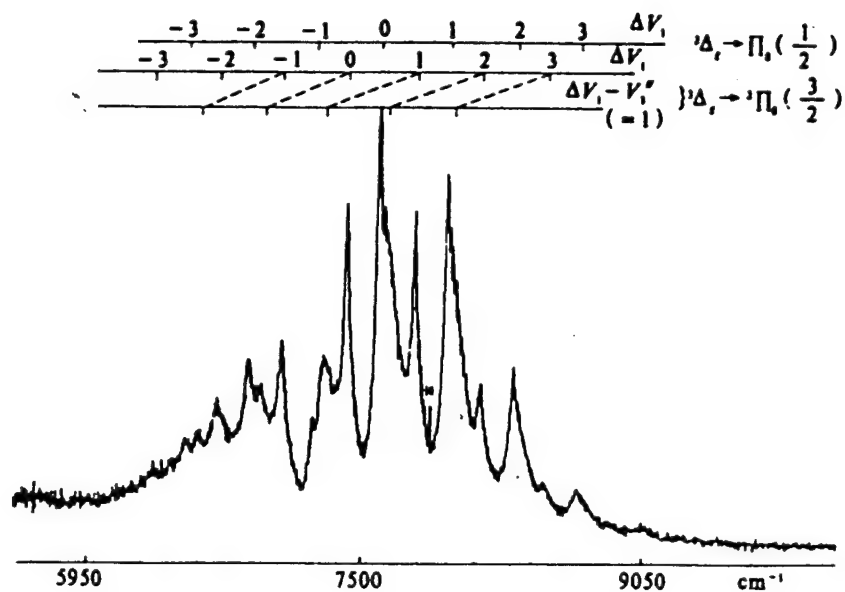

Figure 5. The near-IR emission spectrum with resolution $0.3cm^{-1}$

Table 2. Measured peak energies (in boldface) and their assignments in the near-IR emission spectrum. Uncertainty is $\pm 2.0\,\text{cm}^{-1}$, except where otherwise indicated.

1st sequence (F_1) $^3\Delta_g \rightarrow {}^3\Pi_g\ (j=1/2)$		$F_1 - F_2$ (cm^{-1})	2nd sequence (F_2) $^3\Delta_g \rightarrow {}^3\Pi_g\ (j=3/2)$		$F_2 - F_3$ (cm^{-1})	3rd sequence (F_3) $^3\Delta_g \rightarrow {}^3\Pi_g\ (j=3/2)$	
(cm^{-1})	$(v_1', v_1'')^{b)}$		(cm^{-1})	(v_1', v_1'')		(cm^{-1})	$(v_1', v_1'' v_2'' v_3'')$
6506.6	(0,3)						
364ᶜ⁾							
6870.6	(0,2)	182.1	**6688.5**	(0,2)			
364.1			368.3				
7234.7	(0,1)	177.9	**7056.8**	(0,1)	480.8	**6576**	(0,101)
368.3			368.3			363	
7603.0	(0,0)	177.9	**7425.1**	(0,0)	486.1	**6939**	(0,001)
366.0			372.4			366	
7969.0	(1,0)	171.5	**7797.5**	(1,0)	492.5	**7305**	(1,001)
360.8			354.4			345	
8329.8	(2,0)	177.9	**8151.9**	(2,0)	501.9ᶜ⁾	**7650**ᶜ⁾	(2,001)
351.8			347.6			360	
8681.6	(3,0)	182.1	**8499.5**	(3,0)	489.5ᶜ⁾	**8010**ᶜ⁾	(3,001)

a) Figures located between two boldface figures represent band spacings.

b) Figures in parentheses show the vibrational assignment of the band, e.g. (0,3) means (0, 0, 0)–(3, 0, 0) and (3 , 001) means (3, 0, 0)–(0, 0, 1).

c) Estimated value from the shoulder of a band. Here, the uncertainty will be $\pm 5\,\text{cm}^{-1}$.

Reference Documents

[1]   Yoshida, S., Endo, M., Savano,T., Amano, S., Fujii, H., and Fujioka, T. *J. Appl. Phys.*, 1989, **65**:870.

[2]   Yoshida, S. et al. *Jpn. J. Appl. Phys.*, May 1989, **28**:20.
Yoshida, S. et al. *Appl. Phys. Lett.*, 1989, **54**:2400.
Yoshida, S. et al. *Appl. Phys. Lett.*, 1989, **55**:2707.

[3]   Zhuang, Q., Cui, T., Sang, F., Yuan, Q., Zhang, R., Yang, H., Li, L., Zhu, Q., and Zhang, C. Abstract C Tu Ms CLEO/IQE '90, Advance program:58.
Zhuang, Q. et al. *Conf. Proc.*, 8th Int. Symposium on Gas Flow and Chemical Lasers, Madrid, Spain, 1990.

[4]   Vagin, N.P., Konoshenko, A.F., Kryukov, P.G., Frolov, M.P., and Yuryshev, /504 N.N. *Kvantovaya Elektron.* (Moscow), 1990, **17**(2):204.

[5]   Huang, R., Zhang, R., and Zare, R.N. *Chem. Phys. Lett.*, 1990, **170**:437.

[6]   Cui, T., Xie, X., Qin, Y., Yang, H., and Zhuang, Q. *Chinese J. of Lasers*, 1992, **1**(3):263.

[7]   Cui, T., Wang, Z., Min, X., Wang, D., and Zhuang, Q. *Applied Lasers (Yingyong Jiguang)*, 1992, **12**(4):157.

[8]   Tokuda, T., Fujii, N., Yoshida, S., Shimizu, K., and Tanaka, I. *Chem. Phys. Lett.*, 1990, **174**:385.

[9]   Bacis, R., Bonnet, J., Bouvier, A.J., Churassy, S., Crozet, P., Erba, B., Georges, E., Jouvet, C., Louvet, Y., Lamarre, J., Nota, M., Pigache, D., Ross, A.J., and Setra, M. *Conf. Proc.*, 8th Int. Symposium on Gas Flow and Chemical Lasers, Madrid, Spain, 1990.

[10]   Vagin, N.P., Frolov, M.P., and Yuryshev, N.N. *Kvantovaya Elektron.* (Moscow), 1991, **18**(7):832.

[11]   Bouver, A.J., Bacis, R., Bonnet, J., Churassy, S., Crozet, P., Erba, B., Koffend, J.B., Lamarre, J., Lamrini, M., Pigache, D., and Ross, A.J. *Chem. Phys. Lett.*, 1991, **184**:133.

[12]   Lamarre, J., Bonnet, J., and Pigache, D. Laser M2P, Grenoble, July 9–11, 1991.

[13]   Yang, H.P., Qin, Y., Cui, T.J., Yuan, Q.N., Xie, X.B., Zhuang, Q., and Zhang, C.H. *Chem. Phys. Lett.*, 1992, **191**:130.

[14]   Bacis, R. et al. 47th International Symposium on Molecular Spectroscopy, Columbus, Ohio, USA, June 15–19, 1992.

[15]   Cui, T., Qin, Y., Yang, H., Zhuang, Q. et al. *Data Collection and Processing (Shuju*

Caiji yu Chuli), 1992, **7** (Supplement):224.

[16] Liu, X. Dalian Institute of Chemical Physics, Academia Sinica, 1989 Graduate Student Master's Thesis. 1992.

[17] Lamarre, J. et al. Ninth International Symposium on GCL, Heraklin (Greece), September 21–25, 1992.

DISTRIBUTION LIST

DISTRIBUTION DIRECT TO RECIPIENT

ORGANIZATION	MICROFICHE
BO85 DIA/RTS-2FI	1
C509 BALLOC509 BALLISTIC RES LAB	1
C510 R&T LABS/AVEADCOM	1
C513 ARRADCOM	1
C535 AVRADCOM/TSARCOM	1
C539 TRASANA	1
Q592 FSTC	4
Q619 MSIC REDSTONE	1
Q008 NTIC	1
Q043 AFMIC-IS	1
E404 AEDC/DOF	1
E410 AFDTC/IN	1
E429 SD/IND	1
P005 DOE/ISA/DDI	1
1051 AFIT/LDE	1
PO90 NSA/CDB	1

Microfiche Nbr: FTD95C000621
NAIC-ID(RS)T-0365-95